Foaming of Oils: Effect of Poly(dimethylsiloxanes) and Silica Nanoparticles

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ABSTRACT: Foaming of oils often confronts researchers in food, cosmetics, and petrochemical industries. Destabilization or stabilization of nonaqueous foams is fundamentally crucial for process control and product quality. Antifoams can be a useful method to control excessive foams. Nonetheless, the foaming mechanisms and the selection criteria of the most common antifoam, poly(dimethylsiloxane) (PDMS) oils, are not thoroughly discussed. The study of inorganic colloidal particles as foam stabilizers has drawn particular attention over the past years practically and academically, yet only a small part of literature focuses on nonaqueous foams. For these reasons, we have studied the effects of PDMS oils and silica nanoparticles on the foaming of oils. We find that the performance of silicone oils as crude oil antifoams is firmly related to PDMS viscosity and crude oil composition presumably because the solubilization of PDMS oils in hydrocarbons reduces with increasing viscosity of the polymers and the hydrocarbons. The findings also illustrate that nanoparticle hydrophobicity and concentration are the primary factors for the foam stabilization effect.
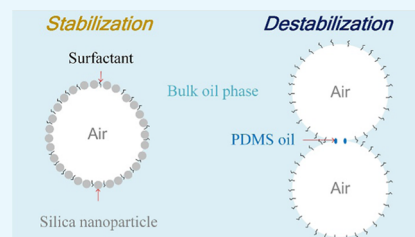
1. INTRODUCTION

Many processes of industrial production produce foam. The existence of foam may adversely affect the safety and economy of the production process. For example, the wet desulfurization plants can experience overflowing foams due to the slurry in the absorbing tower, which is harmful to the stable operation of the desulfurization system.[1] In the pulp and paper industry, the use of cellulose-based materials for papermaking involves stirring and turning the surfactant-containing pulp slurry, which leads to the generation of unwanted bubbles and thus damages the process of papermaking.[2] Similar problems emerge in textile washing, waterborne latex paints and varnishes, and some medical applications.[3] In the oil and gas industry, although it has been reported that annular foam and foamy oil are beneficial for pipeline transportation of heavy oil,[4,5] some stages suffer from foam production. For example, agents for drilling are usually surfactants, which when mixed with the hydrocarbon gases, CO_2 and H_2S, will produce much foam and severely decrease the drilling speed.[6] Another stage of oil and gas production that suffers from problems of excessive foam is gas−oil separation.[7] Crude oil foaming is detrimental to efficient degassing and effective process control. The problematic situation of unwanted foams so commonly arises in the industrial world that we must consider it seriously to overcome these shortages.

Silicone foam control agents prove to be economical and simple and are commonly used in a wide range of industrial processes to suppress and eliminate foams.[8−10] Poly-(dimethylsiloxane) (PDMS) oils are the most common chemical foam control agents, and fluorosilicone fluids are used in some severe cases to provide foam control at small dose levels.[11] PDMS oils are versatile and practical for both aqueous and nonaqueous systems. The selection of ideal PDMS oil type and dose level is dependent on the properties of the foam system. Researchers have proposed several mechanisms governing the behavior of antifoams. Harkins and Robinson defined the spreading and entering coefficients, and Ross introduced the idea of comparing the sign of the spreading coefficient to determine the antifoam activity.[12−14] Garrett pointed out that foam film rupture in some systems was caused by the bridging mechanism and positive values of bridging coefficient corresponded to film rupture.[15,16] Pugh and Denkov rigorously studied the mechanisms of foam destruction by antifoams.[17,18] Denkov tested the entry barriers of oily antifoams with the film-trapping technique. His work demonstrated that the entry barrier was crucial to the antifoam efficiency, and antifoams with low entry barriers (less than 15 Pa) were fast antifoams, which caused film rupture in seconds. Bridging−dewetting or bridging−stretching was the possible mechanism involved in film rupture by fast antifoams.[18] Early literature demonstrated that PDMS oil spreading pressure correlated positively with antifoam efficacy.[19,20] Due to the spread of the PDMS oil on the surface, the surface tension of the foaming system reduced after equilibration. All the above mechanisms regarding antifoam liquid oils for aqueous systems can be extended to nonaqueous systems generally and especially to crude oils.[3] The definitions of the three classical coefficients for estimation of antifoam performance are given in eqs 1−3, where σ is the interfacial tension between two immiscible phases and the subscripts g, a, and o are abbreviations for gas, antifoam, and oil phases.[15] Positive values of these coefficients do not necessarily guarantee foam

Table 1. Oil Properties: Density, API Gravity, Viscosity, Surface Tension, and SARA Composition

oil	1#Murban	2#Murban/Changqing	3#Changqing	4#White oil	5#White oil
ρ at 20 °C (kg/m^3)	740.0	799.0	838.0	851.0	913.0
API gravity	59.7	45.6	37.4	34.8	23.5
μ at 20 °C (mPa s)	16.0	65.0	450.0	16.8	85.5
σ at 20 °C (mN/m)	23.6	25.8	25.6	30.5	32.1
saturates (%)	79.9	81.3	82.6	paraffinic	
aromatics (%)	13.3	12.4	10.8		
asphaltenes (%)	0.5	0.4	0.6		
resins (%)	4.8	4.8	5.3		

Table 2. Antifoam Properties: Density, Viscosity, and Surface Tension

poly(dimethylsiloxane)	ρ at 20 °C (kg/m^3)	μ at 20 °C (mPa s)	σ at 20 °C (mN/m)
S10	963	10	18.88
S50		50	19.67
S150		150	19.98
S250		250	20.13
S350		350	20.19
S500		500	20.27
S1000		1000	20.46

suppression, but they are essential for the application of antifoams, as more positive coefficients are usually linked to more likely antifoaming behavior.[19,21] Other considerations must be accounted for regarding crude oil foams. Differences in sizes of antifoam drops may affect the probability of effectiveness. However, it is hard to predict the size distribution and the aggregation state of the antifoam drops.[22] Additionally, the solubility of the antifoams in the medium and the presence of solids or gels on the lamellae are of cardinal importance.[23,24] There is evidence that the composition of crude oil (including the dissolved low-molecular-weight gaseous components) can affect the solubility of PDMS (and derivatives). Therefore, working with real gaseous components at high pressure and temperature is better at revealing the antifoam performance. Furthermore, the downstream effects of the additive are crucial for the selection of crude oil antifoams.[25,26]

$$E = \sigma_{g/o} + \sigma_{a/o} - \sigma_{g/a} \tag{1}$$

$$S = \sigma_{g/o} - \sigma_{a/o} - \sigma_{g/a} \tag{2}$$

$$B = \sigma_{g/o}{}^2 + \sigma_{a/o}{}^2 - \sigma_{g/a}{}^2 \tag{3}$$

When product purity is of significant concern, antifoams may bring in a source of irreversible contamination. In this regard, mechanical defoaming methods have unique advantages compared to chemical foam-breaking methods. The most common arrangement of mechanical defoaming devices is the rotary unit, such as rotating disks, centrifugal baskets, spinning cones, and cyclones.[27] These devices lack consensus on the ideal design. However, most of the designs involve the use of centrifugal, shear, and impact forces to enhance liquid redistribution.[3] Low-viscosity foams are reported to be successfully destroyed with ultrasound in the textile and dairy industries, whereas this technique is less successful for medium-viscosity foams produced from vinyl chloride based adhesives.[17] A theory held that foam drainage was enhanced when cooperating waves squeezed liquid from the film into the node.[28] Experiments by Winterburn suggested that rupture front breakage dominated the collapse of foam under the influence of ultrasound.[29]

Stabilization of emulsions and foams with particles has long been observed by Ramsden and Picking.[30,31] However, the role of solid particles to stabilize air bubbles in surfactant-free systems has just been elucidated recently.[32−35] The innovative work on phase inversion of particle-stabilized materials from aqueous foam to dry water and from nonaqueous foam to dry oil is done by Binks and Murakami.[36,37] Binks illustrated that phase inversion can be induced by varying the particle hydrophobicity or the air/water ratio. The transitional hydrophobicity is approximately 20% SiOH for fumed silica particles, whereas the preparation of oil marbles (oil in air materials) requires the elaborate design of oil-repellent surfaces by creating surface roughness. Gonzenbach reported an in situ hydrophobization approach to tune surface-wetting properties through short-chain amphiphilic molecules with high solubility in the aqueous phase.[38] He later applied this approach to the modification of particles with different isoelectric points.[39] Thomas suggested that particles of suitable hydrophobicity (33% SiOR) exhibit maximum ability to stabilize air bubbles when a high concentration of NaCl (3 mol/dm^3) was added.[40] Nonaqueous systems stabilized by particles were investigated by Amro, who used either dichlorodimethylsilane-coated fumed silica or organo-modified laponite clay as colloidal particles.[41]

This work aims to explore the effect of PDMS oils as crude oil antifoams and investigate the stabilization of nonaqueous foams by silica particles. We defined four parameters to characterize the effect of PDMS oils and silica nanoparticles on crude oils. The results are significant for understanding and controlling crude oil foams in the oil and gas industry. Furthermore, the study can help understand the role of inorganic colloidal particles on nonaqueous foams. Thus, potential applications in pharmaceuticals and cosmetics can benefit from this study.

2. RESULTS AND DISCUSSION

2.1. Development of the Experimental Program. The crude oil properties are listed in Table 1. We used
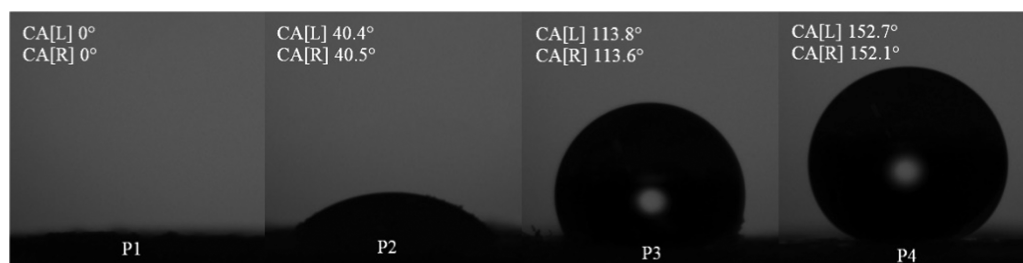
Figure 1. Water drop deposited on the silica nanoparticles with different hydrophobicities.

poly(dimethylsiloxanes) (PDMS oils) of different viscosity as crude oil antifoams. Antifoam properties are given in Table 2. We prepared silica nanoparticles of different hydrophobic grades. It can be seen from Figure 1 that the hydrophobicity of the nanoparticles progressively increases from 0 to roughly 152°, indicating that particle hydrophobicity increases progressively. Figure 2 shows the scanning electron microscopy
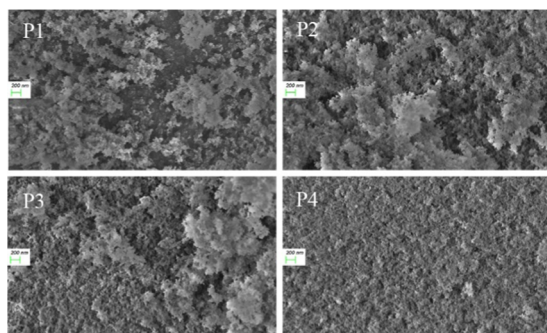

Figure 2. SEM image of the silica nanoparticles with different hydrophobicities.

(SEM) images of the silica nanoparticles with different hydrophobicities. The particles tend to agglomerate in the air due to surface forces.[42] We characterized the stability of the foam by performing the pneumatic test with the apparatus illustrated in Figure 3.[25,43−47]
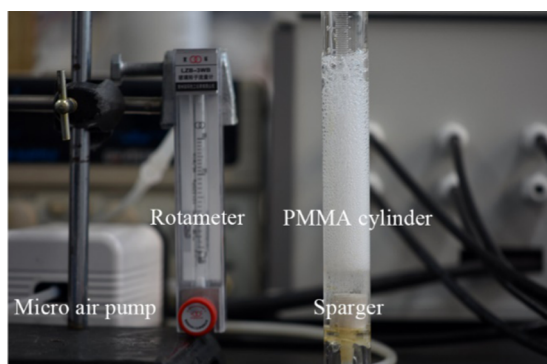

Figure 3. Apparatus for the pneumatic test of foaming of oils.

2.2. Effect of Poly(dimethylsiloxanes). Figure 4 shows the excellent suppression of crude oil foam by homogenizing 5 wt % PDMS S1000 in oil sample 1. Figure 4a shows the evolution of foam volume against time without the additive. Figure 4b shows the equivalent time-lapse images after the homogenization with the additive. The new dispersion system shows a lower level of foamability in contrast.
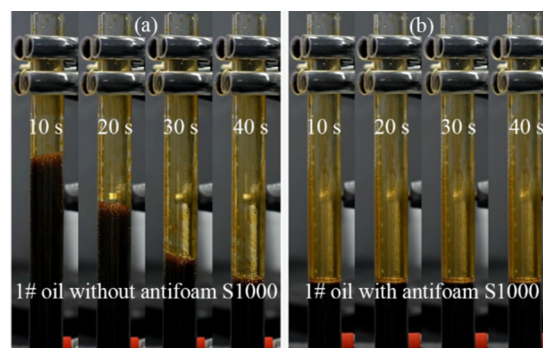

Figure 4. Time-lapse images of foaming of 1 oil without (a) and with (b) PDMS oil S1000.

In Figure 5, the points that are on the right-hand side of the break position indicate viscosity for effective antifoams. Figure 5a shows that antifoamability effect (AE) generally has a positive correlation with PDMS viscosity. The break position in the x-axis marks the transition from ineffective antifoam to effective antifoam. Antifoams S10 and S50 have negative AE, whereas others have positive AE. The critical viscosity, in this case, is the minimum viscosity for PDMS oils to act as effective antifoam. As the viscosity increases from 150 to 1000 mPa s, AE increases from 63 to 94%.

Foam characterizations of 5 wt % poly(dimethylsiloxanes)/oil systems were further conducted to investigate the antifoam performance on crude oils. The antifoamability and destabilization effects correlate positively with poly(dimethylsiloxane) viscosity for all crude oils in general. Antifoam performance on oil sample 1 versus PDMS viscosity is shown in Figure 5b. When PDMS viscosity is 1000 mPa s, AE and DE are more than 90%. The antifoam performance of oil sample 2 as a function of PDMS viscosity is shown in Figure 5c. The critical viscosity is between 10 and 50 mPa s. S150, S500, and S1000 show more than 90% increase in AE and DE. The antifoam performance of oil sample 3 as a function of PDMS viscosity is shown in Figure 5d. The critical viscosity is between 10 and 50 mPa s, and good antifoam performance (both AE and DE are around 90%) is achieved with S150. When the viscosity of the oil sample increases, AE and DE of S50 increase from negative to positive. This trend suggests that the critical viscosity of effective antifoaming PDMS oils may increase with crude oil viscosity.

The antifoam performance as a function of PDMS concentration is shown in Figure 6, which shows that AE and DE are almost directly proportional to the PDMS concentration between 0.1 and 0.5 wt %. It is noteworthy that PDMS oils can be distinguished as fast antifoams (effective in less than a minute) for oil foam inhibition, suggesting that they have low entry barriers.[18] From a
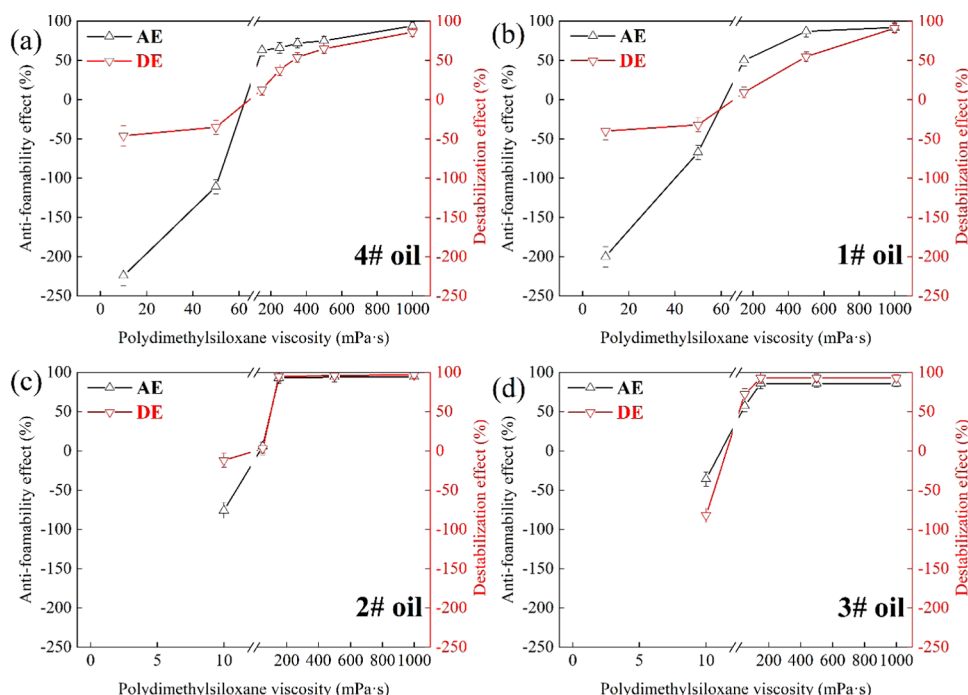
Figure 5. Antifoamability effect and destabilization effect (AE and DE) versus poly(dimethylsiloxane) viscosity: (a) 4 oil, (b) 1 oil, (c) 2 oil, and (d) 3 oil.
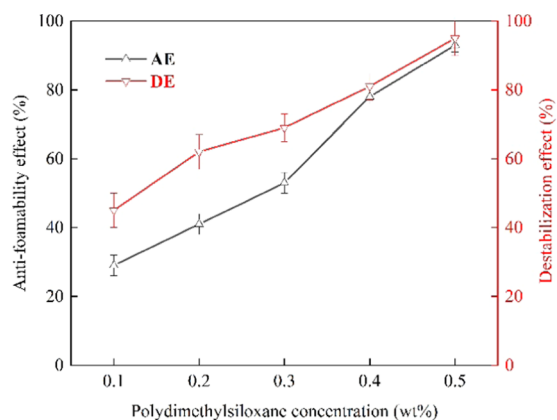

Figure 6. Dependence of the antifoamability effect and destabilization effect on poly(dimethylsiloxane) concentration.

probabilistic point of view, it is speculated that PDMS oil tends to spread on the surface with a higher probability if the antifoam concentration is high. Therefore, the increases in the probability of an antifoam drop arriving in a foam film may explain that the antifoam effect increases with increasing concentration of antifoam. The more dilute the antifoam dispersion, the fewer the drops and the lower the probability of antifoam action. Besides, differences in the sizes of individual drops may affect the probability of effectiveness even when they are present in a foam film.

Some relevant observations are similar to the experimental results in this study. The earliest reference to the PDMS oils as profoamers for nonaqueous foaming systems can be traced back to half a century ago by Shearer.[48] Centers observed a similar phenomenon regarding the profoaming effect of PDMS oils on a synthetic ester turbine lubricant.[49] L'Hostis and Renauld reported increased antifoam effectiveness of PDMS oils with increasing viscosity.[50] Pape reported improved foam

control of crude oil with PDMS oil of molecular weight more than 1 900 000. He cited that antifoam performance on the Ekofisk platform in the North Sea was boosted 4-fold by increasing the PDMS viscosity from 12.5 to 60 Pa s.[51] Callaghan showed that the antifoaming effect of PDMS oil turns to profoaming effect if sufficient short-chain alkanes were added to the dead crude oil.[52]

On the one hand, it was revealed by Mannheimer that the solubilization of PDMS oils in hydrocarbons decreased with increasing viscosity of the hydrocarbons.[53] It can be seen from our test that S50 is the profoaming agent for light 1 oil, whereas it is the antifoaming agent for viscous 3 oil. Our experimental results strongly support the conclusion of Mannheimer in this regard. On the other hand, the solubilization of PDMS oils in hydrocarbons seems to reduce with increasing viscosity of the polymers.[52] Good antifoam effectiveness with viscous PDMS is attributable to the inverse correlation between PDMS solubility in the crude oil and PDMS viscosity according to Pape.[51] Using PDMS antifoams in aqueous media, however, does not involve the complication because the solubility is so low that it is not a problem, where the rate at which the sizes of the antifoam drops decrease to suboptimal dimensions reduces if the antifoam viscosity increases, so that effective antifoam action stands for long periods.

Moreover, the temperature is another crucial point. Shearer demonstrated that the solubility of PDMS in a hydrocarbon lube oil had a positive correlation with temperature, so its antifoaming effect lessened progressively and ultimately became profoaming.[48] Similar behavior is expected when mixing crude oil with PDMS. These observations and explanations combined to show the real advantage of the use of the most viscous PDMS as antifoams.

Callaghan attributed his observations to the miscibility of PDMS with such alkanes.[52] Furthermore, the effect of PDMS became profoaming as the antifoam was solubilized by the

addition of sufficient short-chain alkanes to the dead crude oil. He clarified that solubilization of PDMS oils in hydrocarbons reduced and the antifoam effects persisted at higher concentrations of added short-chain alkanes by increasing the viscosity of the antifoam polymer. The observations of Callaghan served to suggest that the variation of oil compositions can substantially impact antifoam effectiveness of PDMS oils.[52] Thus, it is possible to decrease the antifoam solubility and improve the antifoam effectiveness by degassing a crude oil (lower hydrocarbon components are removed). In contrast, effective antifoams in dead crude oils may be rendered ineffective in live crude oils. He gave a concrete example of this problem where a PDMS oil was effective in the degassed crude oil but ineffective in the live crude oil, presumably because of its lower solubility in the dead oil.[52]

It is notable that the classical coefficients cannot predict the profoaming behavior of the low-viscosity PDMS oils because the antifoam/oil and the antifoam/gas interfacial tensions are approximately the same. The disagreement between the calculations of these coefficients and the real antifoam behavior has been reported for aqueous media and illustrated with the effect of the entry barrier.[18] Unfortunately, presently neither a systematic experimental observation of the wetting behavior of the antifoam drops on crude oils nor a full picture of the dispersion state of PDMS oils in crude oils is available. The available comprehensive analysis on the foaming of oils with direct methods, such as the surface rheological and thin-film methods, was done by Callaghan almost 40 years ago.[44] It is, therefore, necessary to revisit the methods to study this problematic issue with current understanding. Moreover, whether the observations based on the behavior of antifoams in other nonaqueous media can be extrapolated to crude oils is another complication. Thus, it is difficult to assert here the mechanisms in the case of crude oils because the direct optical observations at the lamellae or plateau borders are not accessible.

2.3. Effect of Silica Nanoparticles.
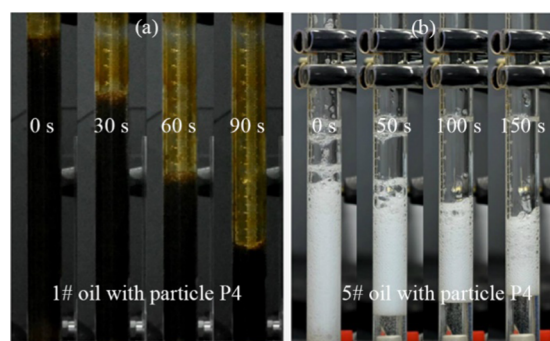Figure 7 shows the stabilization of 1 and 5 oil foams by 0.01 wt % hydrophobic

Figure 7. Stabilization of the 1 oil foams (a) and 5 oil foams (b) by the addition of 0.01 wt % hydrophobic silica nanoparticle P4.

silica nanoparticle P4. The time-lapse images in Figure 7a,7b were taken 10 min and 1 h, respectively, from the onset of the tests when constant foam height was reached, indicating that the dispersion was in equilibrium and the equilibrium rates are not the same for different nonaqueous systems. The persistence of the liquid film up in the cylinder in Figure 7b is good evidence of the increased rigidity of the interface.

The excellent ability of nanoparticles to enhance foamability and increase foam stability is particularly highlighted because

of the high surface area. We found that it took about 1 h for the nanoparticles/oil sample 5 foaming system to reach a constant foam volume because the absorption of the nanoparticles to the oil/air interface was a relatively slow process. Sufficient time must be allowed for the rearrangement and packing of the particles at the oil/air interface.[33] We tried to test the foam/particle systems by gradually reducing the concentration of the particles so that the concentration of the nanoparticles was below the limit defined by the height of the foam column. Foam characterizations of 0.07 wt % nanoparticles/oil system were performed to determine the effect of hydrophobicity of silica nanoparticles on the foamability and foam stability. The profoamability effect (PE) and stabilization effect (SE) of nanoparticles of different hydrophobicities are given in Figure 8. The PE and SE in Figure 8 were calculated
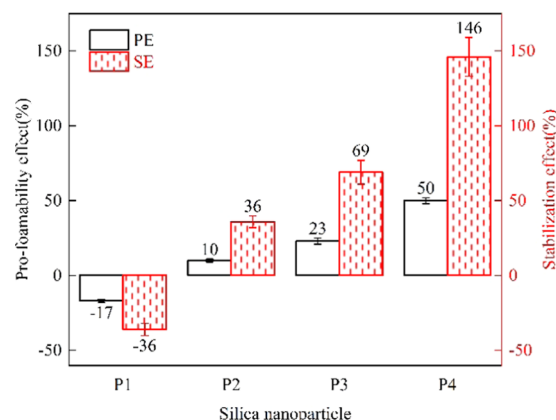

Figure 8. Dependence of the foamability effect and stabilization effect on the hydrophobicity of silica nanoparticles.

half an hour from the onset of the test before a constant foam volume was reached for convenience. The effect of nanoparticle P1 is entirely different from the effect of P2−P4. Nanoparticle P1 does not contribute to the foamability or half-decay time, whereas P2−P4 show remarkable level of ability to increase the foamability and the half-decay time. As the hydrophobicity of silica nanoparticles increases, the PE and SE increase progressively. A positive correlation can be established between PE and SE because they shift from negative to positive concurrently. The difference among results of nanoparticles of different hydrophobicities demonstrates that if the hydrophobicity of the nanoparticles is less than a critical value, the nanoparticles will not stably absorb to the oil/air interface. Among the nanoparticles we prepared, P4 increases the foamability and the half-decay time to a greater extent than other particles. It is anticipated that the energy barrier to absorption of particles to the oil/air interface is reduced progressively as hydrophobicity increases. If absorbed, the nanoparticles form a close-packing layer stabilizing air bubbles against Ostwald ripening. The close-packing layer increases the rigidity of the interface, thus inhibiting film rupture and bubble coalescence.

The effect of nanoparticles as a function of concentration is shown in Figure 9. The PE and SE of nanoparticles P4 at different concentrations were calculated an hour from the onset of the test when the constant foam volume was reached. PE and SE have positive correlations with nanoparticle concentration between 0.002 and 0.03 wt %. Hydrophobic silica nanoparticle with certain surfactants in oil can be useful
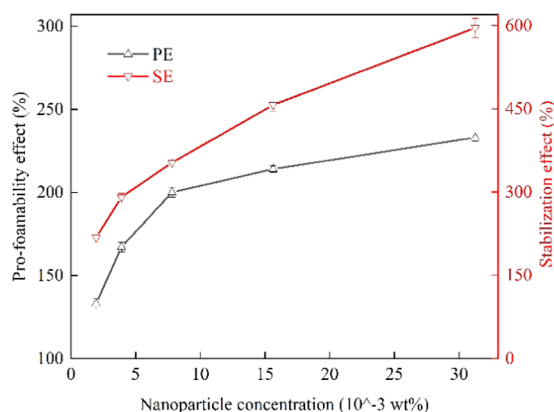
Figure 9. Dependence of the foamability effect and stabilization effect on nanoparticle concentration.

stabilizers of the nonaqueous foam with increased foamability and foam stability (133 and 218%) at a low concentration (0.002 wt %). It is proposed that the increased foamability and foam stability arise from a bridging monolayer/bilayer of close-packing particles or a network of particle aggregates.[54] A higher nanoparticle concentration allows more bubbles to be covered with particle layers or networks. Furthermore, bubbles coated with more particles show an increased stability against disproportionation and coalescence. Thus, the foamability and foam stability have a positive correlation with nanoparticle concentration.

We have only carried out the pneumatic test with air. The test results with air show an interesting aspect of the stabilization effect of the hydrophobic silica nanoparticles, which corresponds with the idea brought out by previous studies that colloidal particles can be foaming agents of oils. The findings clearly illustrate that inorganic solid particles, which accompany the production of crude oil, can be foaming agents apart from asphaltene, resin, and acidic components. The conclusions are probably less satisfying without the depressurization test because the depressurization tests have their limitations. Therefore, there is abundant room for further progress in this area. Also, the selection of foaming surfactants for nonaqueous systems is usually small compared to aqueous systems. In a broad sense, solid particles can be used as foaming agents for nonaqueous systems when necessary.

3. CONCLUSIONS

We have studied the performance of silicone oils as crude oil antifoams. Antifoam efficacy is strongly affected by PDMS viscosity. The effect of silicone oil transitions from stabilization to destabilization when the PDMS viscosity surpasses critical viscosity. Antifoam effectiveness is almost directly proportional to concentration. The classical theory cannot predict the profoaming behavior of the low-viscosity PDMS oils.[9] This observation coincides with some early descriptions, presumably because of the differences in solubility.[48,53] Good antifoam effectiveness with viscous PDMS is attributable to the inverse correlation between PDMS solubility and PDMS or crude oil viscosity.

Nanoparticle hydrophobicity and concentration are the main factors for foam stabilization. Sufficient time must be allowed for the rearrangement and packing of particles at the oil/air interface. It is anticipated that the energy barrier to absorption of particles to the oil/air interface is reduced progressively as hydrophobicity increases, so nanoparticles will not firmly absorb to the oil/air interface when hydrophobicity is under the critical value. The strength of the bridging layers or the networks is greater when nanoparticle concentration is higher, thus stabilizing foam to a greater extent. In food, cosmetics, and petrochemical industries, the illustration and application of particle-stabilized nonaqueous foams are rapidly developing, but other factors, such as the size or type of particles, still await further elucidation.

4. EXPERIMENTAL SECTION

4.1. Fluid Selection. Two crude oils and two mineral oils were chosen as foaming systems. A third crude oil was created by mixing the two crude oils in a 1:1 ratio. When we mixed the two crude oils, no signs of incompatibility appeared. Oil sample 1 was a light crude oil from Murban region. Sample 3 was a slightly heavy crude oil from Changqing, China. We used paraffinic mineral oils 4 and 5 in some tests because they had good foamability without adding chemicals. Oil sample 5 (913 kg/m^3) is heavier than oil sample 4 (851 kg/m^3) and has lower foamability. Oil samples 1, 4, and 5 were good natural foaming liquids, whereas 2 and 3 oils were not; so, 3 vol % sodium abietate (oil-soluble anionic amphiphile) was added into oil samples 2 and 3 to increase their foamability. The surfactant had little impact on oil viscosity. After the preparation, the oils were preserved in a hermetic vessel so that the physicochemical properties of the oils stayed virtually the same.

Viscosity was characterized with the Anton Paar rheometer at 20 °C. The surface tension was measured with the KRÜSS force tensiometer K100 by which ten measurements were automatically performed to obtain the results. The viscosity was characterized by the Anton Parr rheometer MCR302 (concentric cylinder measuring system). The SARA composition for crude oils 1−3 is tested with the NB/SH/T 0509-2010 method (n-heptane for asphaltene precipitation).

4.2. Preparation and Characterization of Silica Nanoparticles. Silica nanoparticles of different hydrophobic grades were prepared by treating hydrophilic silica nanoparticles (99.8% pure, primary diameter 7−40 nm, surface area 200 m^2/g, supplier Aladdin) with different amounts of silylating reagent. The silylating reagent used was dichlorodimethylsilane (96.0% pure, Aladdin). First, hydrophilic silica nanoparticles were heated at 120 °C for 50 min. Silica particles/ethanol system, 4.8 wt %, was gently agitated in a round-bottom flask. Deionized water (5 wt % to silica nanoparticles) and different amounts of dichlorodimethylsilane (5, 7.5, 10, and 20 wt % to silica nanoparticles) were added into the flask, which was heated under reflux (120 °C, 50 min) to increase the rate of silanization. The suspension was then washed with ethanol twice. Silica nanoparticles produced with this method were named P1, P2, P3, and P4 in the ascending order of hydrophobicity.

The contact angles of water on analogous silica plate systems for P1−P4 were measured by optical contact angle goniometer. The surface morphologies of the silica nanoparticles were observed by scanning electron microscope (ZEISS Sigma 500). The sample was stuck onto the conductive adhesive, and a layer of gold was sprayed on the samples under vacuum for SEM scanning.

4.3. Foam Test. The most representative and suitable test for studying crude oil foams is the depressurization test because depressurization or decompression is closely related to how crude oil foams are mainly produced.[7,55] However, there

are some problems with this technique because some oils do not produce any depressurization foam.[56] In our case, oils 1, 2, 3 do not produce foam using the depressurization test.[7] Sufficient time was allowed for saturation. Still, the amount of depressurization foam was ignorable. We have tested the new mixture with surfactant sodium abietate in the depressurization test but still cannot produce an appreciable volume of foam. Additionally, the cleaning procedure is a serious issue because it is difficult to remove the remaining viscous oil from the tubes and the ball valves. Furthermore, we observed the incompatibility of different oils provided that oils were not thoroughly cleaned in the depressurization test. For these reasons, we have not tried to perform the depressurization test. We are aware of the difference between the depressurization test and the pneumatic test, but we can only perform the pneumatic test on the crude oils. In further research, it might be possible to construct the pressurized apparatus with components that are easily disassembled and cleaned to investigate the antifoam performance based on the depressurization method.

The micro air pump generated a continuous air flow, which was then regulated and measured by a rotameter (range 30−300 mL/min). The fine sintered glass sparger (mean pore size 50 μm) was fitted at the bottom of the poly(methyl methacrylate) (PMMA) cylinder (inner diameter 18 mm, height 200 mm). The gas flow rate was maintained at 150 mL/min until a constant foam height was reached. A column of static foam was left to collapse to half of its constant foam volume after a time. A high-resolution camera was used to capture the evolution of foam height against time. Special attention was paid to the reliability of the experimental method by rigorously averaging the results from three consecutive runs. Several measures are taken to keep experimental errors to a minimum. The glassware and PMMA cylinder were cleaned with petroleum ether and then deionized water.

Foaminess $\sum$, Foamability Π, and half-decay time t were used to characterize foam evolution. Foaminess is defined as the ratio of the constant foam volume to the air flow rate. Foamability is defined as the ratio of the constant foam volume to the initial liquid volume.[43] When foam reached a constant volume, the air flow was cut off. Half-decay time is defined as the time when foam height (measured from air/foam interface to foam/bulk liquid interface) collapses to half of the constant foam height.

Throughout the tests, the air flux rate was kept at 150 mL/min. The room temperature was kept at 20 °C. Oil samples 1−4 were used as foaming systems for the test of antifoam performance versus PDMS viscosity. At first, oil sample 4 was tested to find the preliminary results. Then, the other oils were tested to find what they had in common. Oils that are 5 cm in height were placed in the graduated open PMMA cylinder for tests. Then, air was injected into the cylinder via the sparger from the bottom. For the test of antifoam performance versus PDMS concentration, air was injected into the cylinder containing oil sample 2 with different proportions of S150.

For the test of the nanoparticles/oil system, oil sample 5 was used as the foaming liquid because chemical-free oil sample 5 had the least foamability, which ensures that a constant foam height in the presence of silica nanoparticles will not exceed the height of the graduated cylinder. Air was injected into the cylinder containing oil sample 5 of height 4 cm with nanoparticles P1−P4. For the test of nanoparticle concentration, air was injected into the cylinder containing oil sample 5 of height 4 cm with different proportions of nanoparticle P4.

4.4. Characterization of the Effect of PDMS Oils and Silica Nanoparticles.

We have defined four parameters to characterize the effect of PDMS oils and silica nanoparticles on foamability (foam at maximum volume) and half-decay time (foam stability). The capacity of PDMS oil to prevent foam formation and undermine foam stability is its antifoamability and destabilization effect (AE and DE). The ability of nanoparticle to promote foam formation and enhance foam stability is its profoamability and stabilization effect (PE and SE).

We have related AE and DE to the foamability (the maximum quantity of foam that can be created under test conditions) and half-decay time (the time for the foam to collapse to half of its volume). These new indexes AE and DE of PDMS oils were expressed as percentages and characterized by calculating the percentage decrease of foamability and half-decay time (shown in eqs 4 and 5) compared to the cases without the additive.[9] Thus, antifoams can be readily classified according to their index values. Positive values of AE and DE indicate that PDMS oils have an antifoaming effect, whereas nonpositive values of AE and DE suggest that PDMS oils have no antifoaming effect. Theoretically, foamability Π and half-decay time t can be reduced to zero by antifoams. Thus, AE and DE can reach 100% to the maximum. It is worth noting that some researchers have observed that additives may affect different stages of foam life. Thus the half-decay time alone may not be sufficient for characterization of the effectiveness of antifoams. However, we have not observed that additives affect different stages of foam life within the scope of this test. Additionally, some have argued the antifoaming effect should be distinguished from the defoaming effect because a defoamer is used when the foam is produced already and an antifoam is added before the foam tests.

$$AE = \frac{\Pi_{\text{without PDMS}} - \Pi_{\text{with PDMS}}}{\Pi_{\text{without PDMS}}} \times 100\% \tag{4}$$

$$DE = \frac{t_{\text{without PDMS}} - t_{\text{with PDMS}}}{t_{\text{without PDMS}}} \times 100\% \tag{5}$$

Similarly, the PE and SE of silica nanoparticle were determined by calculating the percentage increase of foamability and half-decay time (shown in eqs 6 and 7). Positive values of PE and SE show that the silica nanoparticle has a profoaming effect, whereas nonpositive values of PE and SE show that the silica nanoparticle has no profoaming effect.

$$PE = \frac{\Pi_{\text{with nanoparticle}} - \Pi_{\text{without nanoparticle}}}{\Pi_{\text{without nanoparticle}}} \times 100\% \tag{6}$$

$$SE = \frac{t_{\text{with nanoparticle}} - t_{\text{without nanoparticle}}}{t_{\text{without nanoparticle}}} \times 100\% \tag{7}$$

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Notes

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